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DIVERGENCE OF PERSISTENT LENGTH OF A SEMIFLEXIBLE HOMOPOLYMER CHAIN IN THE STIFF CHAIN LIMIT

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We revisit analytical calculation [Mishra et al., Physica A **323** (2003) 453 and Mishra, NewYork Sci. J. **3** (1) (2010) 32] of the persistent length of a semiflexible homopolymer chain in the extremely stiff chain limit, $k \to 0$, where, k is the stiffness of the chain, for the directed walk lattice model in two and three dimensions. Our study for the two-dimensional (square and rectangular) and three-dimensional (cubic) lattice case clearly indicates that the persistent length diverges according to the expression $(1-g_c)^{-1}$, where g_c is the critical value of the step fugacity required for polymerization of an infinitely long linear semiflexible homopolymer chain, and nature of the divergence is independent of the space dimension. This is obviously true because, in the case of extremely-stiff chain limit, the polymer chain is a one-dimensional object and its shape is like a rigid rod.

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1. Introduction

The persistent length of a polymer chain measures correlations in the orientation of the segments of the chain along its length. In other words, the persistent length is a measure of the distance along the chain length at which the configuration of the chain on an average has memory of the orientation of its specific segment. The bending rigidity and thus the persistent length is a consequence of the short range atomic and molecular interactions present in the polymer chain. Since, the persistent length is stemming from the bending rigidity of the polymer chain, it can exhibit enormous variation in the magnitude. Therefore, if the persistent length associated with the polymer chain is much smaller than the overall length of the chain, such a chain is said to be flexible and stiffness of such a chain is unity. When the stiffness of the chain is approaching to zero, the persistent length of such a chain becomes comparable to its length and the chain is said to be rigid. However, if the stiffness of the chain has value between 0 and 1, the chain is said to be semi-flexible. Actin filaments, microtubules, DNA, protein and collagen are examples of the semiflexible polymers. The persistent length plays an important role in describing elastic properties of a semiflexible polymer chain and also plays a vital role in developing the theory of polyelectrolyte solutions.

Due to the excluded volume effect, a self-avoiding polymer chain has memory of its specific segment and initial bias persists along the walk of the chain up to a finite distance (for flexible chains) from initial step of the chain. Grassberger [1] initially discussed this problem and showed that the persistent length of a two-dimensional self-avoiding flexible polymer chain diverges with a power law. Later, Redner and Privman [2] suggested that this divergence is logarithmic. However, through MC studies [3], it has been shown that the persistent length could be fitted by a power law and by a logarithmic function. Eisenberg and Baram [4] demonstrated and confirmed that the persistent length of a flexible polymer chain converges to a finite value. The situation is different in the case when polymer chain is semiflexible, and in the extremely stiff chain limit, the persistent length of a semiflexible polymer chain diverges.

The aim of the present report is to take into account correlations prevailing between two distant segments of an extremely rigid polymer chain of an infinitely long length in the bulk and to demonstrate through simple calculations that the persistent length of such a polymer chain, when expressed in terms of critical value of step fugacity in the extremely stiff chain limit (i.e. $k \to 0$), diverges as a simple pole, and the nature of the divergence is independent of space dimensionality.

This report is organized as follows: In Sec. 2, we define briefly the directed walk model and revisit the results of calculation of the persistent length for two-dimensional (square and rectangular) and three-dimensional (cubic) lattice to investigate the divergence of the persistent length of an infinitely long linear semiflexible homopolymer chain in the extremely stiff chain limit. Finally, in Sec. 3, we conclude the discussion by summarizing the results obtained.

2. Model and method of calculations

We consider following two cases of directedness [5] of the polymer chain for square, rectangular and cubic lattices: In the case (i), the partially-directed self-avoiding walk (PDSAW) model, the walker is allowed to walk along $\pm y$ and $+x$ directions on a square or a rectangular lattice, while in the cubic lattice case, walker is allowed to walk along $\pm y$, $+x$ and $+z$ directions. In the case (ii), the fully directed self-avoiding walk (FDSAW) model, the walker is allowed to take steps along $+x$, $+y$ directions in the square and rectangular lattice case, while along $+x$, $+y$ and $+z$

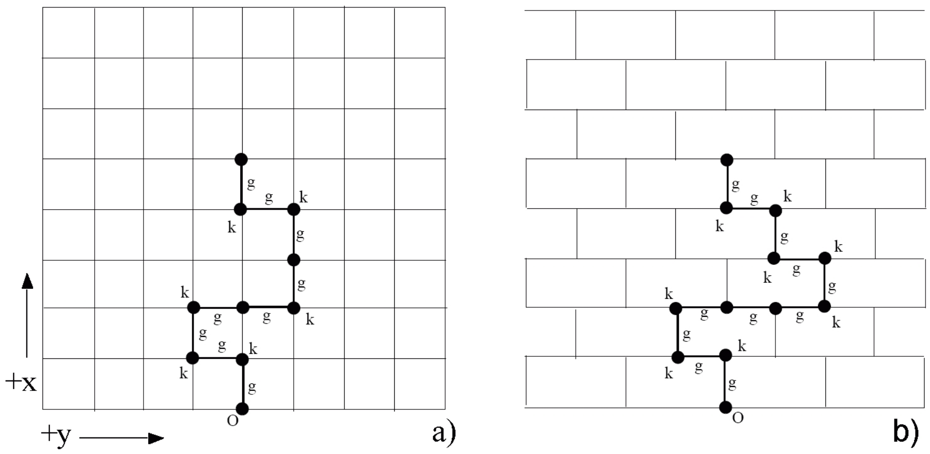

Fig. 1. a) A partially-directed self-avoiding walk of a linear semiflexible polymer chain is shown on a square lattice of 9 steps, and b) on a two-dimensional rectangular lattice of 11 steps. The step fugacity of each step is shown by g, k [$= \exp(-\beta\epsilon_b)$] is the stiffness of the polymer chain, ϵ_b is the value of the bending energy required to produce one bend in the chain and β [$= 1/(k_BT)$] is the inverse of thermal energy. The Boltzmann weight of the walk shown in figure a) is g^9k^6 and in figure b) is $g^{11}k^8$.

directions for the case of a cubic lattice. A partially-directed self-avoiding walk is shown graphically on a two-dimensional rectangular and a square lattice in Fig. 1.

The partition function of the chain is defined as follows

$$Z(g,k) = \sum_{N=0}^{N=\infty} \sum_{\text{over all walks of N steps}} g^N k^{N_b}, \tag{1}$$

where, N_b is the number of bends in a walk of a polymer chain of N steps (monomers) and g is the fugacity associated with each step (monomer). The partition function of the chain is calculated [6, 7] by us using method of generating function technique [5].

The persistent length is defined [Mishra et al. [6]] as an average length of the polymer chain between two successive bends, i. e.

$$l_p = \frac{< L >}{< N_b >} = \left(g \frac{\partial log[Z(g,k)]}{\partial g} \right) \bigg/ \left(k \frac{\partial log[Z(g,k)]}{\partial k} \right),$$

where the length of the chain is $L = Na$, a being the lattice parameter and N is the number of monomers in the chain. We have taken the value of the lattice parameter unity for the sake of simplicity.

2.1. *PDSAW model on a square lattice*

The partition function of a linear semiflexible homopolymer chain for this model is written as [6]

$$Z_{PD-S}(g,k) = \frac{(4k-3)g^2 + 3g}{1 - 2g + g^2 - 2g^2k^2} \,,$$

where g is the step fugacity and k is the stiffness weight associated with each bend of the polymer chain.

The critical value of the step fugacity required for polymerization of an infinitely long linear semiflexible homopolymer chain is determined from the singularity of the partition function. The critical value of the step fugacity for partially-directed self-avoiding walk model of the chain on a square lattice is written in terms of k as [6]

$$g_c = \frac{1}{1 + \sqrt{2}k} \,.$$

This allows us to write k in terms of g_c as

$$k = \frac{1 - g_c}{\sqrt{2}g_c} \,.$$

The persistent length of the polymer chain for the PDSAW model on a square lattice can be written as [6]

$$l_p = \frac{3 + 2\sqrt{2}}{4 + 3\sqrt{2}} \left[\sqrt{2} + \frac{1}{k} \right] . \tag{2}$$

Substituting

$$k = \frac{1 - g_c}{\sqrt{2}g_c}$$

in Eq. (2), we obtain the expression for the persistent length as

$$l_p = (1 - g_c)^{-1}. \tag{3}$$

2.2. *FDSAW model on a square lattice*

For a fully-directed self-avoiding walk model on a square lattice, the partition function of the chain is written as [6]

$$Z_{FD-S}(g,k) = \frac{2g}{1 - (1+k)g} \,,$$

while [6]

$$g_c = \frac{1}{1+k} \, .$$

Therefore, we have the expression for k in terms of g_c as $k = (1-g_c)/g_c$, while the persistent length for this case is, $l_p = 1 + k^{-1}$ [6]. Substituting the value of k in terms of g_c, we get also for this case

$$l_p = (1-g_c)^{-1}. \tag{4}$$

2.3. *PDSAW model on a two-dimensional rectangular lattice*

We have considered a rectangular lattice which has lattice parameter one unit along the x-axis and two units along the y-axis. This rectangular lattice can be derived from a two-dimensional hexagonal lattice and the lattice is shown in Fig. 1b). The partition function of the polymer chain for this case is written as [7]

$$Z_{PD-R}(g,k) = \frac{3g + 2g^2 + 2g^2k - g^3 + 4g^3k - 4g^3k^2}{1 - g^2 - 2g^2k^2} \, .$$

In the case of a two-dimensional rectangular lattice, critical value of the step fugacity for polymerization of an infinitely long linear semiflexible homopolymer chain is written in terms of k as [7]

$$g_c = \frac{1}{\sqrt{1+2k^2}}.$$

In other words, k in terms of g_c is written as

$$k = \frac{1-{g_c}^2}{2{g_c}^2},$$

while the persistent length has dependence on k as, $l_p = 1 + 1/2k^2$ for the PDSAW model on a rectangular lattice. The persistent length (on substitution of k in terms of g_c) is re-written in terms of g_c as,

$$l_p = \frac{1}{(1+g_c)(1-g_c)} \, . \tag{5}$$

2.4. *FDSAW model on a two-dimensional rectangular lattice*

The partition function of the polymer chain for the FDSAW model on a two-dimensional rectangular lattice is [7]

$$Z_{FD-R}(g,k) = \frac{2g + g^2 + g^2k - g^3 + 2g^3k - g^3k^2}{1 - g^2 - g^2k^2} \, ,$$

and we have [7]

$$g_c = \frac{1}{\sqrt{1+k^2}} ,$$

from the singularity of the partition function. In this case, k in terms of g_c is written as

$$k = \frac{1-{g_c}^2}{{g_c}^2} ,$$

and $l_p = 1+1/k^2$ for the FDSAW model on a rectangular lattice in two dimensions. On substitution of k in terms of g_c for the FDSAW model on a two-dimensional rectangular lattice, we get

$$l_p = \frac{1}{(1+g_c)(1-g_c)} . \tag{6}$$

2.5. PDSAW model on a cubic lattice

The partition function of the polymer chain for the partially-directed self-avoiding walk model is [6]

$$Z_{PD-C}(g,k) = \frac{(6k-4)g^2+4g}{(1+k-4k^2)g^2-(k+2)g+1} .$$

In this case the persistent length of the polymer chain is written as [6]

$$l_p = \frac{2u_1[k^{-2}+k^{-1}-4]}{(1-\sqrt{17}+2k^{-1})u_2+(85+21\sqrt{17})k^{-2}} , \tag{7}$$

where

$$u_1 = 85+19\sqrt{17}-(102+26\sqrt{17})k^{-1}+(34+8\sqrt{17})k^{-2}$$

and

$$u_2 = 204+52\sqrt{17}-(272+64\sqrt{17})k^{-1}.$$

The critical value of the step fugacity for this case is [6]

$$g_c = \frac{k+2-\sqrt{17}k}{2(k+1-4k^2)} .$$

For this case too, we follow the method discussed above and substitute

$$k = \frac{(1-g_c)(\sqrt{17}-1)}{8g_c}$$

to obtain,

$$l_p = (1 - g_c)^{-1}. \tag{8}$$

In this case, dependence of the persistent length on k (as shown in Eq. (7)) is more involved than in the cases discussed in subsections (2.1 − 2.4), and expression for the persistent length reduces to a simple form, as we have discussed in subsections (2.1 − 2.4), when the persistent length is expressed in terms of g_c, i.e. Eq. (8).

2.6. FDSAW model on a cubic lattice

The partition function of the polymer chain for the FDSAW model on a cubic lattice is written as [6]

$$Z_{FD-C}(g,k) = \frac{3g}{1-(1+2k)g}$$

The critical value of the step fugacity is

$$g_c = \frac{1}{(1+2k)}$$

and the persistent length is [6]

$$l_p = 1 + \frac{1}{2k}$$

for the FDSAW model on a cubic lattice. In this case, too, (on substitution of $k = (1 - g_c)/2g_c$ in the expression for the persistent length) we obtain,

$$l_p = (1 - g_c)^{-1}\,. \tag{9}$$

3. Conclusions

We have used the definition of Mishra et al. [6] to investigate the nature of the divergence of the persistent length of an infinitely long linear semiflexible homopolymer chain in the extremely stiff chain limit, i.e. when $k \to 0$. In this limit, the polymer chain is a one-dimensional object and average length of the polymer chain between its two successive bends diverges as $(1 - g_c)^{-1}$. In other words, the persistent length diverges as

$$l_p \sim (1 - g_c)^{-1} \sim \frac{1}{k^q}\,,$$

(where q is an integer) for the extremely stiff chain limit.

When the persistent length is expressed in terms of k, the constant of proportionality will depend on the lattice dimension and model. The constant of proportionality will have a different value for the isotropic model and the directed walk model. However, when the persistent length is expressed in terms of g_c, we expect that the nature of the divergence of an average distance between two successive bends of the polymer chain will remain the same for directed and undirected self-avoiding walk models, and constant of proportionality will have a different value for the isotropic (undirected) model and the directed walk model. The nature of the divergence is identical for partially- and fully-directed walk models of the polymer chain for two- and three-dimensional lattices. This is due to the fact that in the extremely stiff chain limit the polymer chain is a one-dimensional object and its shape is like a rigid rod.

The qualitative nature of variation of the persistent length with stiffness of the chain has similar variation for directed and isotropic self-avoiding walk models in two and three dimensions. However, exact value of the persistent length of the chain will depend on space dimensions and type of model (directed or isotropic) chosen to enumerate walks of the chain [8].

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DIVERGENCIJA POSTOJANE DULJINE POLUFLEKSIBILNOG HOMOPOLIMERNOG LANCA U GRANICI KRUTOG LANCA

Obnavljamo analitički račun [Mishra et al., Physica A **323** (2003) 453 i Mishra, NewYork Sci. J. **3** (1) (2010) 32] za postojanu duljinu polufleksibilnog homopolimernog lanca u granici krajnje krutog lanca, $k \to 0$, gdje je k krutost lanca, za model rešetke s usmjerenim hodom u dvije i tri dimenzije. Proučavanje dvodimenzijske (kvadratne i pravokutne) i trodimenzijske (kubične) rešetke jasno pokazuje da postojana duljina divergira kao $(1 - g_c)^{-1}$, gdje je g_c nepostojanost potrebna za polimerizaciju beskonačno dugog linearnog polufleksibilnog homopolimernog lanca, i priroda divergencije ne ovisi o prostornoj dimenziji. To je očito tako jer u slučaju krajnje krutog lanca, polimerski lanac je jednodimenzijski predmet i on ima oblik krutog štapa.